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Date of Application: November 13, 2002

Application Number: Japanese Patent Application No. 2002-329126

Applicant(s): SHIN-ETSU CHEMICAL CO., LTD.
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December 1, 2003

Commissioner,
Patent Office Yasuo IMAI
(seal)

Certificate No. 2003-3099027

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Motoaki IWABUCHI et al.
Serial No.: 10/706,863
Filing Date: November 12, 2003
For: COMPOSITION FOR FORMING POROUS FILM, POROUS FILM AND METHOD FOR FORMING THE SAME, INTERLEVEL INSULATOR FILM, AND SEMICONDUCTOR DEVICE

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks
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Sir:

Hidefumi KAWAMURA residing at c/o OKUYAMA & CO., 8th Floor, Akasaka Noa Bldg., 2-ban 12-go, Akasaka 3-chome, Minato-ku, Tokyo 107-0052, Japan declares:

(1) that he knows well both the Japanese and English Languages;

(2) that he translated the attached specification and claims of U.S. Patent Application Serial No. 10/706,863 from Japanese to English;

(3) that the attached English translation is a true and correct translation of the Japanese text filed on November 12, 2003 to the best of his knowledge and belief; and

(4) that all statements made of his own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 USC 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

Hidefumi Kawamura

Date: June 18, 2004

Hidefumi KAWAMURA

TITLE OF THE INVENTION

COMPOSITION FOR FORMING POROUS FILM, POROUS FILM AND METHOD FOR FORMING THE SAME, INTERLEVEL INSULATOR FILM, AND SEMICONDUCTOR DEVICE

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims priority to Japanese Patent Application No. 2002-329126, filed November 13, 2002, the disclosure of which is incorporated herein by reference in its entirely.

BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to a composition for film formation, which can be formed into a porous film that excels in dielectric properties, adhesion, film consistency and mechanical strength, and has reduced absorption; a porous film and a method for forming the same; and a semiconductor device, which contains the porous film inside.

2. Description of the related art

In the fabrication of semiconductor integrated circuits, as the circuits are packed tighter, an increase in interconnection capacitance, which is a parasitic capacitance between metal interconnections, leads to an increase in interconnection delay time, thereby hindering the enhancement of the performance of semiconductor circuits. The

interconnection delay time is called an RC delay, which is in proportion to the product of the electric resistance of the metal interconnections and the capacitance between the interconnections. Reducing the interconnection delay time requires reducing the resistance of metal interconnections or the interconnection capacitance. The reduction in the interconnection capacitance can prevent a densely packed semiconductor device from causing an interconnection delay, thereby realizing faster semiconductor device with reduced power consumption.

One method for reducing interconnection capacitance is to reduce the relative permittivity (dielectric constant) of an interlevel insulator film disposed between metal interconnections. As such an insulator film with a low relative permittivity, it has been considered to use a porous film instead of a silicon oxide film, which has been used conventionally. A porous film can be said to be the only practical film as a material which has potential to have a relative permittivity (dielectric constant) of 2.0 or less, and various methods for forming a porous film have been proposed

In a first method for forming a porous film as described in Japanese Patent Provisional Publication Nos. 2001-2993, 13-98218 and 13-115021, a composition comprising a thermally unstable organic resin component and a siloxane

polymer is synthesized, is applied on the substrate to form a coating film, and then treated thermally for decomposing and volatilizing the organic resin component so that a number of pores are formed in the film.

In a second method for forming a porous film as described in Japanese Patent Provisional Publication Nos. 2001-131479 and 2001-80915, it is known to carry out processing as follows: a silica sol solution is applied onto a substrate by coating or using a CVD method so as to form a wet gel; and then the silica sol is subjected to a condensation reaction while restricting volume reduction by controlling the speed of the evaporation of the solvent from the wet gel.

In a third method for forming a porous film as described in WO 00/12640 pamphlet, it is known that a silica micro-particle solution is applied on a substrate to form a coating film, and then the coating film is sintered to form a number of micro-pores between silica micro-particles.

However, these methods have respective major drawbacks as follows.

In the first method for forming a porous film, although the high compatibility between the siloxane polymer and the organic component is required from the coating step to the hardening step in order to make the pores small, there is a problem that the compatibility between the siloxane polymer

and the organic resin is poor.

In the second method for forming a porous film, the speed control of the evaporation of the solvent from the wet gel requires a special type of coating device, which increases the cost. In addition, a significant amount of silanol remains on the surface of the micro-pores, which must be silanized because otherwise hygroscopicity is high and the film quality decreases. The silanization makes the process more complicated. In the case where a wet gel is formed by the CVD process, it is necessary to use a special type of CVD device, which is different from the plasma CVD device generally used in the semiconductor process, thereby also increasing the cost.

In the third method for forming a porous film, because the diameter of the pores is determined by the accumulation structure of the silica micro-particles, it becomes very large. This makes it difficult to set the relative permittivity (dielectric constant) of the porous film to 2 or below.

As mentioned above, because the conventional material makes the pore diameter larger during the formation of porous film, there is a problem that the film has difficult in having low dielectric constant. There is also a problem that the cost for forming porous film having fine pores becomes higher. Further, when porous film produced by conventional

material is used as an insulator film in multi-level interconnects of the semiconductor device, there is a problem that the mechanical strength required for the semiconductor processing is not obtained.

Thus, when the dielectric constant of the porous film used as an insulator film in multi-level interconnects of the semiconductor device is high, the RC delay increases. Consequently, there is a large problem that the performance of the semiconductor device (high speed and low power consumption) has not been improved. There is also a problem that the low mechanical strength of the porous film leads to the lowered reliability of the semiconductor device.

SUMMARY OF THE INVENTION

The purpose of this invention is to provide a composition for forming porous film which can form a porous film having practical mechanical strength in a simple and low cost process, a method for forming the film and a porous film.

The purpose of this invention is also to provide an inexpensive, high-performing and highly reliable semiconductor device comprising internal porous film having excellent mechanical strength and low dielectric constant which can be produced at a low cost and is formable by the composition for forming porous film.

Silica-based porous film is formed by removing a

thermally decomposable compound from the composition in which a silica precursor and the the thermally decomposable compound called "porogen" are uniformly distributed and finely scattered, while leaving a silica skeleton. The inventors have found that when the compatibility of the silica precursor and the porogen is poor, there are pores having larger diameters or no pores formed due to the shrinkage in the direction of thickness. It is believed that it is because the porogen is not uniformly distributed in the film which has been formed by hardening the silica precursor. It is also believed even if the porogen may have been uniformly distributed in the film, the functional group which is responsible for the compatibility with the porogen decreases so that the porogen phase appears as the silica precursor hardens. Accordingly, it is considered to make the silica precursor be bonded to the group will become the porogen in order to prevent the phase separation of the porogen. However, in the recent semiconductor process, the temperature for the decomposition and volatilization of porogen has been required to be lower and then it becomes necessary to form the silica skeleton at a low temperature. However, the silica precursor that has been bonded to the porogen has difficulty in being hardened and does not become porous because the temperature for hardening the silica precursor is higher than the decomposition temperature of the

porogen.

On the other hand, the silica precursor typically contains Si-OH and Si-O(alkyl) wherein the alkyl means a alkyl group and forms a siloxane network through hydrolysis and dehydration condensation as shown below. It is found that the condensation requires as high as 250°C or more without catalyst, and it is carried out more effectively at the lower temperature in the presence of acid or base catalyst so that the film having high hardness can be formed. However, when the acid or base catalyst is added to the composition, the condensation reaction can progress even below room temperature. Thus, there is a problem that the storage stability of the composition is damaged remarkably.

The inventors have solved the problem by adding to the composition an acid or base generator for generating the acid or base by the thermal decomposition. More specifically, they have found that hydrolysis of alkoxysilane and condensation of silanol as shown in Formulas (6) and (7) are accelerated by acid or base catalyst generated by thermal decomposition so that the formation of silica skeleton is completed below the decomposition temperature of the porogen. They have also found that because the acid and base generator for generating the acid or base by its thermal decomposition is neutral before the decomposition, it does not adversely affect the storage stability of the composition comprising

the silica precursor.

$$\text{Si-OR}^6 + H_2O \xrightarrow[\text{catalyst}]{} \text{Si-OH} \quad (6)$$

$$\text{Si-OH} + \text{Si-OH or Si-OR}^7 \xrightarrow[\text{catalyst}]{} \text{Si-O-Si} \quad (7)$$

wherein R^6 represents a monovalent hydrocarbon group which may be substituted or unsubstituted; R^7 represents a monovalent hydrocarbon group which may be substituted or unsubstituted and which may be same as or different from R^6 of the Equation (6).

Based on these findings, according to the invention, provided is a composition for forming film in which the acid or base generator for generating acid or base by its thermal decomposition (hereinafter, referred to as the acid or base generator or as Component (B)) is added to a composition comprising a chemically modified silica precursor by being bonded to the porogen and an unmodified silica precursor. Provided also is a method for forming porous film comprising a step of applying said composition on a substrate to form a film and a step of heating the film at or above the decomposition temperature of Component (B), preferably at or above the decomposition temperature of monovalent hydrocarbon

group of the hydrolysate of silane compound represented by Formula (2) below wherein the monovalent group may be a long chain alkyl group which may be substituted or non-substituted.

The hydrolysate of the hydrolysable silane (hereinafter, referred to also as Component (B)) is a polymer which is obtainable by hydrolyzing and condensing one or more silane compounds represented by Formula (1):

$$(R^1)_aSi(R^2)_{4-a} \qquad (1)$$

wherein R^1 represents a straight chain or branched monovalent hydrocarbon having 6 to 20 carbons which may be substituted or unsubstituted and when there are R^1s, the R^1s each may be independently same or different; R^2 represents a hydrolysable group and when there are R^2s, the R^2s each may be independently same or different; and a is an integer of 1 to 3.

Component (A) to be used in the invention may be preferably a polymer having number-average molecular weight of 100 or more which is obtainable by hydrolyzing and co-condensing one or more silane compounds represented by Formula (1) and one more silane compounds represented by Formula (2):

$$(R^3)_bSi(R^4)_{4-b} \qquad (2)$$

wherein R^3 represents a straight chain or branched monovalent hydrocarbon having 1 to 5 carbons which may be substituted or unsubstituted and when there are R^3s, the R^3s each may be

independently same or different; R^4 represents a hydrolysable group and when there are R^4s, the R^4s each may be independently same or different; and b is an integer of 0 to 3.

According to the invention, a method for producing a composition for forming film is provided as well as porous film.

According to the invention, a semiconductor device comprising an internal porous film formed by a composition comprising a silane polymer and an acid or base generator for generating acid or base by its thermal decomposition is provided.

The silane polymer may be preferably polymer obtainable by hydrolyzing and condensing one or more silane compounds represented by Formula (1):

$$(R^1)_aSi(R^2)_{4-a} \qquad (1)$$

wherein R^1 represents a straight chain or branched monovalent hydrocarbon having 6 to 20 carbons which may be substituted or unsubstituted and when there are R^1s, the R^1s each may be independently same or different; R^2 represents a hydrolysable group and when there are R^2s, the R^2s each may be independently same or different; and a is an integer of 1 to 3.

Consequently, the semiconductor device comprising the inexpensive porous film having high mechanical strength and

low dielectric constant can be provided.

The silane polymer may be preferably polymer obtainable by hydrolyzing and co-condensing one or more silane compounds represented by Formula (1) and one more silane compounds represented by Formula (2), Formulas (1) and (2) being:

$$(R^1)_aSi(R^2)_{4-a} \qquad (1)$$

$$(R^3)_bSi(R^4)_{4-b} \qquad (2)$$

wherein R^1 represents a straight chain or branched monovalent hydrocarbon having 6 to 20 carbons which may be substituted or unsubstituted and when there are R^1s, the R^1s each may be independently same or different; R^2 represents a hydrolysable group and when there are R^2s, the R^2s each may be independently same or different; and a is an integer of 1 to 3; R^3 represents a straight chain or branched monovalent hydrocarbon having 1 to 5 carbons which may be substituted or unsubstituted and when there are R^3s, the R^3s each may be independently same or different; R^4 represents a hydrolysable group and when there are R^4s, the R^4s each may be independently same or different; and b is an integer of 0 to 3.

The silane polymer may be preferably a hydrolysate having number-average molecular weight of 100 or more and comprising a silanol group, and in said polymer 30 to 80 mol% of structural units derived from said silane compound represented by Formula (2) is represented by Formula (3):

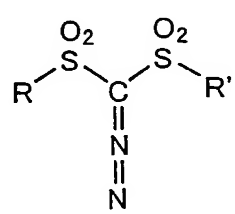
$$Si(OH)_c(R^5)_{4-c} \qquad (3)$$

wherein R^5 represents a siloxane residue or R^3, and c is an integer of 1 or 2.

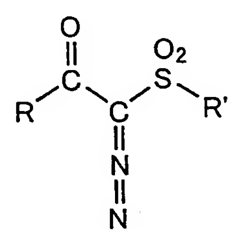
Consequently, the semiconductor device comprising the inexpensive porous film having high mechanical strength and low dielectric constant can be provided.

The decomposition temperature of said acid or base generator may preferably lower than that of R^1 of said polymer. Further, the acid or base generator may preferably have decomposition temperature of 250°C or less. Consequently, the semiconductor device comprising the inexpensive porous film having high mechanical strength and low dielectric constant can be provided.

The acid or base generator may be preferably a diazo compound represented by Formula (4) or (5):



(4)



(5)

wherein R and R′ each independently represents an alkyl group, an aromatic group, an aralkyl group or a fluoroalkyl group and R and R′ may be same or different.

When the diazo compound represented by Formula (4) or

(5) is used as the acid or base generator, it can decompose at lower temperature than the decomposition temperature of R^1 of the silane polymer which is obtained through hydrolysis and condensation.

According to the semiconductor device of the invention, the semiconductor device comprising the multi-level interconnects containing an internal porous film securing the mechanical strength and having low dielectric constant can be realized. Because of lower dielectric constant of the insulator film, the parasitic capacitance of the area around the multi-level interconnects is decreased, leading to the high-speed operation and low power consumption of the semiconductor device. The increased mechanical strength of the film can enhance the reliability of the semiconductor device.

Moreover, in the semiconductor device of the invention, the porous film may be preferably between metal interconnections in a same layer of multi-level interconnects, or may be between upper and lower metal interconnection layers. Consequently, high-performing and highly reliable semiconductor can be realized.

The use of the composition for forming porous film of the invention can provide porous film having low dielectric constant, being flat and uniform, and having high mechanical strength. The porous film is best suitable for the insulator